

(12) PATENT ABRIDGMENT (11) Document No. AU-B-46006/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 619363

(54) Title
PROCESS FOR SEPARATING COPPER FROM AQUEOUS BASE

International Patent Classification(s)
 (51)⁴ **C22B 015/00 B01D 011/04 C07C 13¹/00**
 (51)⁵ **C07C 251/40 C22B 003/30**

(21) Application No. : **46006/89** (22) Application Date : **08.12.89**

(30) Priority Data

(31) Number (32) Date (33) Country
3841673 10.12.88 DE FEDERAL REPUBLIC OF GERMANY

(43) Publication Date : **14.06.90**

(44) Publication Date of Accepted Application : **23.01.92**

(7i) Applicant(s)
HOECHST AKTIENGESELLSCHAFT

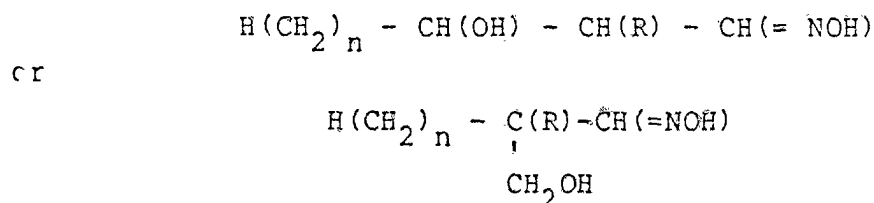
(72) Inventor(s)
DR. JURGEN WEBER; DR. PETER LAPPE; WERNER DE WIN

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
US 4500494
US 4314976
US 3674464

(57) Claim

1. A process for separating copper from aqueous base solutions by extraction with an oxime, which is dissolved in an organic solvent immiscible in water, characterised in that a compound of the following general formulae is used as an oxime:



where R stands for an alkyl group with 2 to 8 carbon atoms and n denotes an integer from 2 to 10.

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2. A process according to claim 1, characterised in that 3-hydroxy-2-ethylhexanaloxime, 3-hydroxy-2-heptylundecanaloxime or 2-hydroxymethyl-2-methylpentanaloxime is used as the oxime.

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952-69

619363

Form 10

COMPLETE SPECIFICATION

(ORIGINAL)

Class

Int. Class

Application Number:

Lodged:

Complete Specification Lodged:

Accepted:

Published:

Priority :

Related Art :

Name of Applicant : HOECHST AKTIENGESELLSCHAFT

Address of Applicant : 50 Bruningstrasse, D-6230 Frankfurt/Main 80,
Federal Republic of Germany.

Actual Inventor : JURGEN WEBER, PETER LAPPE and WERNER DE WIN.

Address for Service : WATERMARK PATENT & TRADEMARK ATTORNEYS.
~~50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000~~XX

"The Atrium", 290 Burwood Road, Hawthorn. Victoria 3122.
Complete Specification for the invention entitled: Australia.

PROCESS FOR SEPARATING COPPER FROM AQUEOUS BASE

The following statement is a full description of this invention, including the best method of performing it known to

us

Process for separating copper from aqueous base solutions

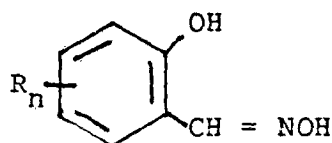
The invention relates to a process for liquid-liquid extraction of copper from aqueous base solutions. Solutions of water-insoluble oximes in water-insoluble organic solvents are used as extracting agents.

The use of oximes for extracting copper from aqueous solutions is known.

Thus the DE-OS 15 33 079 teaches a process for selective extraction of copper from solutions with a low pH value. The extracting agent used is a mixture of a 2-hydroxybenzophenone oxime and an aliphatic alpha-hydroxyoxime, which are dissolved in a hydrophobic organic solvent. Adding the aliphatic oxime increases the rate of copper extraction.

The DE-OS 21 25 095 relates to the selective extraction of copper, nickel, iron and/or cobalt salts from aqueous solutions with a ketoxime which is dissolved in kerosene, toluene or xylene. The ketoxime corresponds to the general formula $R-C(=NOH)-R^1$, R being a straight-chain or branched alkyl radical with 7 to 11 carbon atoms and R^1 denoting a phenyl group carrying an OH group in ortho position to the radical $R-C(=NOH_2)-$ and another R^2 group. Good results are achieved with solutions containing the copper salt in concentrations of 0.05 to 0.5 moles/litre. A low pH value increases the yield of copper extracted.

According to the DE-OS 23 34 901, compounds of the general formula



dissolved in organic solvents which are immiscible in water are used for extracting copper and optionally also iron, cobalt and zinc from their aqueous solutions. The process is particularly suitable for separating copper from iron-containing solutions.

The DE-OS 26 12 505 describes the separation of copper from acidic aqueous solutions by means of liquid-liquid extraction with a mixture of a hydroxyoxime of the general formula $A-C(=NOH)-R$, where A denotes an aromatic radical substituted in the ortho position by an OH group and R stands for a hydrogen atom or an aliphatic radical, and/or a 2-hydroxybenzophenone oxime as well as another oxime, which are dissolved in an organic solvent.

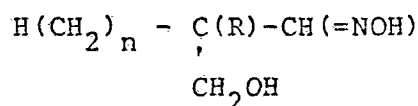
The known processes for separating copper from aqueous solutions by extraction with oximes do not fulfil all practical requirements. In particular, the completeness of the separation and/or the cost-effectiveness of the extracting agent are not always solved satisfactorily.

Therefore the task consisted in developing a process for extracting copper from aqueous solutions which avoids the above shortcomings and permits near-complete and economic separation of copper.

The above task is solved by a process for separating copper from aqueous base solutions by extraction with an oxime, which is dissolved in an organic solvent immiscible in water. The new procedure is characterised in that a compound of the following general formulae is used as an oxime:



or



where R stands for an alkyl group with 2 to 8 carbon atoms and n denotes an integer from 2 to 10.

The process according to the invention is characterised by the use of readily accessible oximes which permit nearly complete separation of the copper from its aqueous solution in only a few extraction steps.

Of the oximes which are covered by the general formulae, 3-hydroxy-2-ethylhexanaloxime, 3-hydroxy-2-heptylundecanaloxime and

2-hydroxymethyl-2-methylpentanaloxime have proved particularly useful.

In order to prepare the oximes, the hydroxyaldehydes on which they are based are taken. The 3-hydroxy-2-alkylalkanals are obtained from alkanals by aldol addition, appropriately in the presence of a secondary amine as a catalyst. Thus, for example, it is particularly easy to obtain 3-hydroxy-2-ethylhexanal from n-butanal with di-n-butylamine as a catalyst. According to a process described in the DE-PS 19 57 591, 2-alkyl-2-hydroxy-methylalkanals can be prepared from 2-alkylalkanals and formaldehyde in the presence of tertiary amines.

After being separated from the reaction mixture, the aldol can be reacted, without further cleaning, with a hydroxylamine salt, e.g. the sulfate, and alkali hydroxide in aqueous phase. Optionally, the reaction can take place with a gently warmed reaction mixture and then the raw water-insoluble oxime separated from the water phase. The oxime is concentrated in the known manner, e.g. using a thin-film evaporator. It has been shown that it is not necessary to use the oxime in extremely pure form. Products of technical purity, which mainly contain the oximes according to the invention but also by-products from aldol addition and oxime formation, have also proved to be admirably suitable for copper separation. Mixtures of the oximes used according to the invention can also be employed.

To perform the extraction, the oximes are dissolved in organic solvents which are immiscible in water. The following are suitable: aliphatic hydrocarbons such as hexane and heptane, low-boiling crude oil fractions of the kerosene type (boiling range 175 to 325°C), aromatic hydrocarbons such as benzene, toluene, xylene, chlorinated hydrocarbons such as chloroform, carbon tetrachloride, dichloroethane as well as higher alcohols such as n-octanol, isooctanol, isononanol, decanol and isotridecanol. Isononanol and isotridecanol are particularly suitable solvents.

The concentration of the extracting agent in the extraction solution can be varied within wide ranges. It is generally 0.02 to 2 moles/litre, preferably 0.1 to 0.15 moles/litre of extraction solution. It can be recommendable to improve the solubility of the oxime in the organic solvent by adding a solubiliser, in particular for the preparation of more highly concentrated solutions. Suitable solubilisers for this purpose are, for example, aliphatic alcohols with 6 to 18 carbon atoms such as hexanol, n-octanol, i-octanol, isononanol, decanol, isotridecanol. The solubilisers are normally used in an amount of 1 to 25 % by weight, preferably 2 to 10 % by weight, related to the weight of the extraction solution. Mixtures of hydrocarbons and the above-mentioned alcohols have proved particularly useful.

The copper to be separated is present as a salt in aqueous solution. The concentration of the copper in this solution can range from approx. 0.1 to approx. 1.0 % by weight, in particular 0.1 to 0.3 % by weight, related to the copper salt solution.

An important feature of the process according to the invention is that the copper salt is extracted from a base solution. Its pH value is ^{preferably} 8 to 12, ^{more} preferably 9 to 10. With acidic solutions, it is expedient to adjust the desired pH value by adding ammonia, with solutions whose pH value is greater than 12 by adding mineral acids, in particular sulfuric acid.

The ratio of the volumes of extraction solution and copper salt solution can vary within wide ranges during extraction. In general the volume ratio of organic extraction solution to aqueous copper salt solution is 1 : 10 to 5 : 1, preferably 1 : 1.

The extraction temperature can also vary widely. Normally extraction takes place at 15 to 60°C and preferably at 20 to 40°C.

Extraction is performed in the known apparatus for liquid-liquid extractions. The aqueous solution to be extracted and the non-aqueous extraction solution are brought into contact continuously or discontinuously by mixing in cocurrent or countercurrent. After the extraction equilibrium has been established, the phases are separated from each other and worked up.

The copper is recovered from the organic phase according to state-of-the-art processes. The claimed invention recommends that the organic copper-containing solution be treated with a diluted



aqueous mineral acid solution whose pH value is less than 2, preferably approx. 1. After separation of the aqueous and organic phases the organic phase is again brought into contact with a mineral acid solution with the same pH value to absorb more copper from the organic solution. The reactions with the mineral acid take place at temperatures of 10 to 30°C, preferably 15 to 25°C. Examples of mineral acids which are used are hydrochloric acid, sulfuric acid, phosphoric acid or nitric acid; sulfuric acid is preferred. The concentration of the mineral acid in the diluted aqueous solution is 0.1 to 3.0 moles/litre, preferably 1.5 to 2.0 moles of acid/litre and in particular 0.3 to 0.7 moles/litre. Other substances which are known to improve extraction with oximes can be added to the oxime solution used for extraction. For example, tertiary carboxylic acids of the general formula $R^1R^2C(CH_3).COOH$, R^1 being an alkyl radical with 1 to 3 carbon atoms and R^2 an alkyl radical with 3 to 5 carbon atoms, have proved useful.

The new process is characterised by rapid establishment of the extraction equilibrium and almost complete extraction of the copper.

The following examples explain the invention without restricting it to these special embodiments.

Preparation of 3-hydroxy-2-ethylhexanaloxime

6.45 g of di-n-butylamine (0.05 moles) are stirred into distilled water in a nitrogen atmosphere and heated to 40°C. Then 720 g of n-butanal (10 moles) and another 6.45 g of di-n-butylamine are added over a period of 30 minutes. The temperature increases to 60°C. After all the reactants have been added, the mixture is stirred for another hour at 60°C. The mixture is cooled to 40°C and the phases separated. 724 g of raw aldol with the following composition (in % by weight, related to the mixture) are obtained:

n-Butanal	27.8
Di-n-butylamine	1.8
2-Ethylhexenal	1.4
3-Hydroxy-2-ethylhexanal	57.0
Components	4.0
Water	8.0

The basis for the preparation of 3-hydroxy-2-ethylhexanaloxime is the raw aldehyde.

624 g of hydroxylamine sulfate (3.8 moles) are dissolved in 2458 g of water and heated with stirring in a nitrogen atmosphere to 40°C. Then 904 g of 33.6 % sodium hydroxide solution (7.6 moles of NaOH) are added. Over a period of 30 minutes 720 g of raw aldol are poured into this solution while it is heated to 80°C. The solution is left to after-react for 1 hour and then the phases are separated, 788 g of raw oxime with the following composition (in % by weight) are obtained:

n-Butanaloxime	25.0
2-Ethylhexenaloxime	1.0
3-Hydroxy-2-ethylhexanaloxime	58.8
Components	4.4
Water	10.8

By using a thin-film evaporator at 130°C und 13.3 hPa 3-hydroxy-2-ethylhexanaloxime of approx. 95 % purity is isolated from the raw oxime und used as such for extraction in the presence of an isononanol-kerosene mixture.

Example 1

100 ml of a copper sulfate solution (Cu content: 209.7 mg corresp. to 3.3 mmoles), which has been adjusted to a pH value of 10 by adding ammonia, are extracted five times in each case for 2 minutes, each time with 100 ml of a solution of 0.01 moles of 3-hydroxy-2-ethylhexanaloxime (about 95 %) and 0.023 moles of isononanol in 94 ml of kerosene. The course of the extraction is given below:

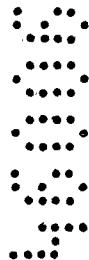
	Cu in the extraction solution (mg)	Cu related to feed (in %)
1st stage	124.1	59.2
2nd stage	25.2	12.0
3rd stage	10.7	5.1
4th stage	6.2	2.9
5th stage	5.2	2.5
Total extracted:	171.4	81.7

Examples 2 to 6

The following examples describe extraction of a copper salt solution containing 33 mmols of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per litre. The extracting agent used is a raw product containing about 60 % by weight of 3-hydroxy-2-ethylhexanaloxime to which the solvents and solubilisers previously described have been added to further improve the hydrophobic properties.

In each case 100 ml of the copper sulfate solution are intensively mixed five times in each case with 100 ml of extraction solution and for 2 minutes each time. Then the phases are separated and the Cu content in the organic solution is determined.

The pH value in the copper sulfate solution is adjusted by adding ammonia. In the examples 2, 3 and 4 Na_2SO_4 is also added to the copper salt solution.



Example	2	3	4	5	6
Cu solution (mg Cu/l)	2097	2097	2097	2097	2097
pH value	10	10	10	10	9
Na ₂ SO ₄ added(mole/l)	-	0.5	-	0.5	0.5
<u>Extraction sol. (mole/l)</u>					
n-Butanaloxime	0.12	0.08	0.16	0.020	0.04
2-Ethylhexanaloxime	0.002	0.002	0.004	0.0005	0.001
3-Hydroxyoxime	0.1	0.1	0.2	0.025	0.05
Isononyl alcohol	0.4	0.4	0.8	0.1	to 1 l
Kerosene	topped up to 1 litre				-
Cu:3-Hydroxyoxime (in moles)	1:3	1:3.3	1:6	1:0.75	1:1.5
Cu:tot. Oxime (in moles)	1:6.7	1:5.5	1:11	1:1.26	1:2.7
<u>Organic phase</u>					
1st stage					
mg Cu/% of feed	195.2 98.3	187.5 89.7	137.5 65.7	127.4 60.9	88 42.0
2nd stage					
mg Cu/% of feed	9 4.3	15.3 7.3	21.3 10.2	20.8 9.9	29 13.8
3rd stage					
mg Cu/% of feed	2.5 1.2	0.9 0.4	8.8 4.2	5.7 2.7	3.9 1.8
4th stage					
mg Cu/% of feed	1.2 0.6	0.8 0.4	6.5 3.1	2.2 1.1	0.7 0.3
5th stage					
mg Cu/% of feed	0.8 0.4	0.6 0.3	5.3 2.5	0.9 0.4	0.4 0.2
Yield					
mg Cu/% of feed	208.7 99.8	205.1 97.8	179.4 85.7	156.9 75	122 58.2

Example 7

For regeneration purposes the copper-containing oxime solution is treated with an aqueous mineral acid solution. 400 ml of extraction solution (Cu content: 136.4 mg) are mixed with 500 ml of water; the pH value is adjusted to 1 by adding sulfuric acid. After 5 minutes of intensive mixing and subsequent phase separation, the aqueous solution contains 135 mg of Cu, i.e. 98.7 % of the copper contained in the organic phase is recovered.

Example 8

300 ml of regenerated oxime solution from example 7 are intensively mixed for 5 minutes with 400 ml of a copper salt solution (Cu content: 839 mg/l) whose pH value is 10. After single extraction the extraction solution contains 680.8 mg of Cu, i.e. 81.1 % of the copper contained in the aqueous solution is separated.

Preparation of 3-hydroxy-2-heptylundecanaloxime

3.23 g of di-n-butylamine (0.025 moles) are stirred into distilled water in a nitrogen atmosphere and heated to 40°C. Then 710 g of n-nonanal (5 moles) and another 3.23 g of di-n-butylamine are added. The temperature rises to 50°C. After all the reactants have been added, the mixture is stirred for 1 hour at 60°C. It is then cooled to 40°C and the phases are separated. 713 g of raw aldol with the following composition (in % by weight, related to the mixture) are obtained:

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Di-n-butylamine	0.4
2-Methyloctanal	2.3
n-Nonanal	24.2
2-Heptylundecenal	10.9
3-Hydroxy-2-heptylundecanal	61.4
Water	0.8

Thin-film distillation of the raw aldol leads to a product with the following composition (in % by weight):

First runnings	1.6
Nonanal	15.2
2-Heptyl-2-undecenal	12.5
3-Hydroxy-2-heptylundecanal	70.4
Last runnings	0.3

This product is used for preparing 3-hydroxy-2-heptylundecanaloxime.

98.5 g of hydroxylamine sulfate (0.6 moles) are dissolved in 171 g of water and heated to 40°C in a nitrogen atmosphere with stirring. Then 120 g of 33.3 % sodium hydroxide solution (1 mole of NaOH) are added. Over a period of 30 minutes 141.8 g of aldol are poured into this solution which is simultaneously heated to 80°C. After 1 hour of after-reaction the phases are separated. 141.3 g of raw oxime with the following composition (in % by weight) are obtained:

Nonanaloxime	16.1
2-Heptyl-2-undecenaloxime	12.7
3-Hydroxy-2-heptylundecanaloxime	71.2

This raw oxime is used for the extraction described below:

Example 9

100 ml of a copper sulfate solution (Cu content: 209.7 mg/l, corresp. to 3.3 mmoles), adjusted to a pH value of 10 by adding ammonia, are extracted five times in each case for 2 minutes, each time with 100 ml of a solution of 0.01 moles of 3-hydroxy-2-heptylundecanaloxime and 0.02 moles of isononanol dissolved in kerosene. The course of the extraction is given below:

	Cu in the extraction solution (mg/l)	Cu related to the feed (in %)
1st stage	130	61.9
2nd stage	36.2	17.3
3rd stage	24.4	11.6
4th stage	13.7	6.5
5th stage	5.4	2.5
Total extracted	209.7	100

Preparation of 2-hydroxymethyl-2-methylpentanaloxime

71,65 g of tri-n-propylamine (0.5 moles) are heated to 60°C in a nitrogen atmosphere together with 424.5 g of formalin solution (37.1 % $\approx$ 5.25 moles). Over a period of 20 minutes 501 g of 2-methylpentanal (5 moles) are added and the mixture heated to 100°C for 6 hours with return flow. After cooling to room temperature the phases are separated. 750 g of raw aldol with the following composition (in % by weight, related to the mixture) are obtained:

Formaldehyde	1.4
Tri-n-propylamine	7.6
2-Methylpentanal	3.9
2-Hydroxymethyl-2-methylpentanal	74.3
Component 1	4.4
Component 2	3.7
Water	4.7

Fractionated distillation of the raw aldol leads to a product with the following composition (in % by weight, related to the mixture):

First runnings	3.5
2-Methylpentanal	3.2
Intermediate runnings	3.2
2-Hydroxymethyl-2-methylpentanal	90.1

This product is used for preparing 2-hydroxymethyl-2-methylpentanaloxime.

50.9 g of hydroxylamine sulfate (0.31 moles) are dissolved in 88.4 g of water and heated to 40°C in a nitrogen atmosphere with stirring. Then 60 g of 33.3 % sodium hydroxide solution (0.5 moles) are added. Over a period of 30 minutes 72.2 g of the aldol fraction (0.5 moles) are poured into this solution which is simultaneously heated to 80°C. After the solution has been left to after-react for 1 hour, the phases are separated. 88.7 g of raw oxime with the following composition (in % by weight) are obtained:

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First runnings	0.2
2-Methylpentanaloxime	2.9
2-Hydroxymethyl-2-methylpentanal	2.2
Intermediate runnings	5.3
2-Hydroxymethyl-2-methylpentanaloxime	80.5
Water	8.9

Example 10

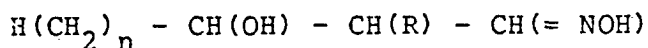
100 ml of a copper sulfate solution (Cu content: 203.7 mg/l, corresp. to 3.3 mmoles), adjusted to a pH value of 10 by adding ammonia, are extracted five times in each case for 2 minutes, each time with 100 ml of a solution of 0.01 moles of 2-hydroxymethyl-2-methylpentanaloxime and 0.02 moles of isononanol in kerosene. The course of the extraction is given below:

	Cu in the extraction solution (mg/l)	Cu related to the feed (in %)
1st stage	130	61.3
2nd stage	7.6	3.6
3rd stage	2.8	1.3
4th stage	1.6	0.8
5th stage	1.0	0.5
Total extracted:	143	68.2

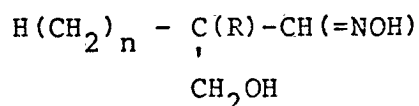
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

~~xxPatentxx~~claims

1. A process for separating copper from aqueous base solutions by extraction with an oxime, which is dissolved in an organic solvent immiscible in water, characterised in that a compound of the following general formulae is used as an oxime:



or



where R stands for an alkyl group with 2 to 8 carbon atoms and n denotes an integer from 2 to 10.

2. A process according to claim 1, characterised in that 3-hydroxy-2-ethylhexanaloxime, 3-hydroxy-2-heptylundecanaloxime or 2-hydroxymethyl-2-methylpentanaloxime is used as the oxime.
3. A process according to claim 1 or 2, characterised in that aliphatic or aromatic hydrocarbons, chlorinated hydrocarbons or higher alcohols are used as the organic solvent.
4. A process according to claim 3, characterised in that the organic solvents contain a solubiliser.

5. A process according to claim 4, characterised in that the solubiliser is an aliphatic alcohol with 6 to 18 carbon atoms.
6. A process according to any one of the claims 1 to 5, characterised in that the concentration of the oxime in the solution is 0.02 to 2 moles/litre.
7. A process according to any one of the claims 1 to 6, characterised in that the pH value of the copper salt solution is 8 to 12.
8. A process according to any one of the claims 1 to 6, characterised in that the pH value of the copper salt solution is 9 to 10.
9. A process according to any one of the claims 1 to 7, characterised in that the volume ratio of oxime solution to aqueous copper salt solution is 1 : 10 to 5 : 1.
10. A process according to any one of the claims 1 to 7, characterised in that the volume ratio of oxime solution to aqueous copper salt solution is 1 : 10 to 1 : 1.
11. A process according to any one of the claims 1 to 8, characterised in that extraction takes place at temperatures of 15 to 60°C.
12. A process according to any one of the claims 1 to 8, characterised in that extraction takes place at temperatures of 20 to 40°C.

DATED this 17th day of October, 1991.

HOECHST AKTIENGESELLSCHAFT

WATERMARK PATENT & TRADEMARK ATTORNEYS
THE ATRIUM
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

AU004600689.wpc

